

Using principal component analysis to distinguish sources of radioactivity and nitrates contamination in Southern Tunisian groundwater samples

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ABSTRACT

The manuscript discusses using Principal Component Analysis (PCA) to distinguish the sources of radioactive and nitrate contamination in 33 groundwater samples from southern Tunisia. The study focuses on the Gafsa basin, an area known for its phosphate mining activities and significant agricultural use, both of which contribute to the contamination of groundwater resources. The radioactivity in the water is primarily attributed to phosphate mining and deep groundwater sources from the North Western Sahara Aquifer System (NWSAS). Additionally, the nitrate contamination is largely due to agricultural runoff, though secondary sources related to phosphate mining are also considered.

Through the application of PCA, the study was able to classify the groundwater samples into different groups based on their contamination sources: phosphate mining, combined agricultural and mining activities, fossil geothermal waters, and low-agricultural areas. The PCA revealed that samples most affected by anthropogenic activities exhibited high levels of radium and nitrate, with contamination patterns correlating with specific environmental and chemical factors.

This analysis underscores the complexity of groundwater contamination in the region and highlights the need for targeted mitigation strategies to address radioactive and nitrate pollution in southern Tunisia. The study provides critical insights for managing water quality in areas with similar environmental challenges.

1. Introduction

Tunisia is one of the world's leading phosphate producers, ranking fifth in 2010. Natural phosphate and fertilizer derivatives are exported to nearly 50 countries. The Gafsa Basin, located in Southern Tunisia, encompasses most of the country's phosphate mining activities. The Palaeogene (mainly Eocene) and Early/Late Cretaceous formations constitute the main geological outcrops in the study area (Hamed, 2013; Nasri et al., 2024). The geological units of the Metlaoui Group, which hosts the phosphate series of the Gafsa-(Metlaoui) Basin, are attributed

to the Eocene. This primarily includes three formations: i) the Thelja Formation, characterized by dolomitic deposits alternating with gypsum and marl; ii) the Chouabine Formation, which comprises four phosphate subunits; iii) the Kef-Eddour Formation, consists of marl-phosphate alternations framed by two limestone bars (Hamed, 2013; Nasri et al., 2024).

Phosphates are known to contain a range of stable radionuclides, mainly belonging to the ²³⁸U series and its decay products (Machraoui et al., 2024). Tunisian phosphate rock, in particular, contains between 45 and 140 ppm of uranium (Khleifia et al., 2013). The radioactivity

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contamination of groundwater resources in the study area is primarily attributed to (Hamed et al., 2024): i) phosphate mining, storage, and processing; ii) deep fossil and thermal groundwater from the trans-boundary North Western Sahara Aquifer System (NWSAS). In Tunisia, the annual production of phosphogypsum, a radioactive byproduct of phosphate mining (Ajam et al., 2009), is estimated at approximately 10 million tons. In addition, groundwater in the Gafsa basin (Fig. 1a) exhibits high nitrate concentrations, often exceeding the drinking water standard of 50 mg/L (WHO, 2022), with a mean value of 168 mg/L (Hamed et al., 2013). These elevated nitrate levels indicate a significant contribution from return flow waters in the recharge of the unconfined aquifer. Ammonium nitrate, liquid fertilizer, and other commercial complex nitrogen fertilizers are used on a large scale in agricultural areas where flood irrigation is applied (Hamed et al., 2013, 2024). Secondary nitrate contamination from the oxidation of products like mono-/di-ammonium phosphate, ammonium nitrate, or explosives like Ammonium Nitrate Fuel Oil (ANFO), used during phosphate mining, is also possible (Issaoui, 2022; Mokadem et al., 2016).

In this short communication, we aim to distinguish the sources of radioactive and nitrate contamination in 33 groundwater samples from southern Tunisia using Principal Component Analysis (PCA). To our knowledge, no studies have been conducted on water to identify the source of radioactivity and nitrates utilising this approach, either in Tunisia or elsewhere.

2. Material and methods

The radioactivity concentration (Bq/l) of ^{226}Ra , ^{228}Ra , ^{228}Th , ^{234}U , ^{238}U , and the gamma radioactivity rate (mSv/y) from 33 previously published samples (Hamed et al., 2024) are re-elaborated within a dataset that also includes novel data: major cationic and anionic constituents (Ca, Mg, Na, K, Cl, SO_4 , NO_3 , HCO_3), physico-chemical parameters (pH, temperature), and other factors (TDS, depth) (Supplementary file 1). Based on their origin, the samples were divided into four classes: phosphate mining, agricultural and phosphate mining, fossil geothermal, and low agricultural area.

3. Results and discussion

Concerning the chemical parameters, all groundwater samples exhibit a Na–Cl chemistry, except for sample #20, which shows a Mg (Na–Cl) composition. Due to this compositional homogeneity, the Langelier-Ludwig diagram does not reveal distinct groupings of samples (Fig. 1b). However, the distribution of samples falls between the field of chloride-sulfate alkaline waters and the field of chloride-sulfate earth-alkaline waters, the latter represented by the typical composition of the Complex Terminal (CT) aquifer (Upper Cretaceous and Mio-Plio-Quaternary). The waters of the fossil geothermal group belong to the deep Continental Intercalaire (CI) sandstone aquifer (Lower Cretaceous of NWSAS), whose salinity is due to the dissolution of evaporite intercalations (Edmunds et al., 2003). The chemical indistinguishability of

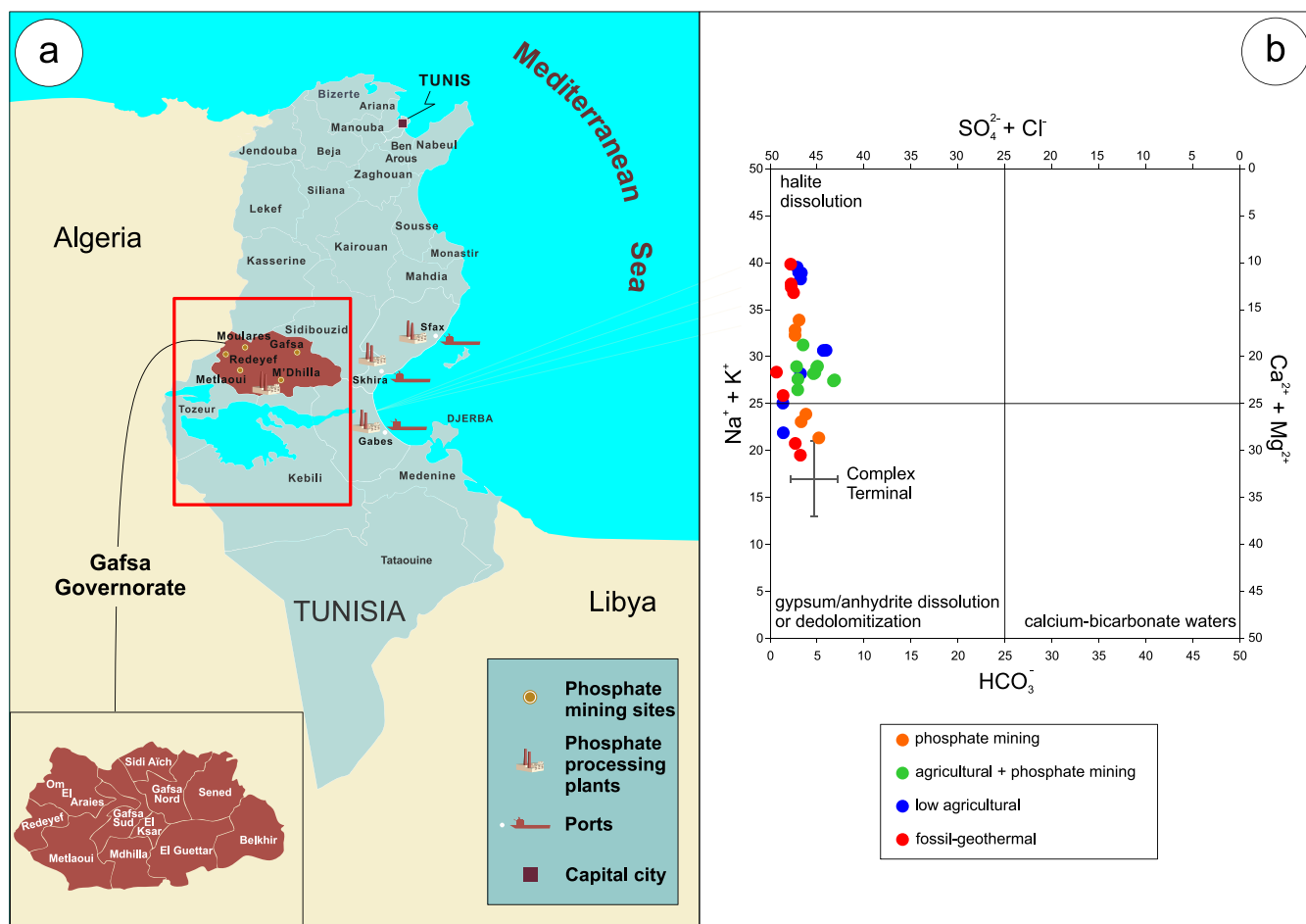


Fig. 1. a) Map of the study area (modified from GTC, 2012). Phosphate deposits in Tunisia are located in the mining area of Gafsa Governorate. The study area is outlined in red. b) Langelier-Ludwig plot of the groundwater samples from this study (data in eq/L). The mean composition and standard deviation (error bars) of the Complex Terminal aquifer in the Northern Gafsa basin are included for comparison (Mokadem et al., 2016). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the groundwater is also mainly because the Mio-Plio-Quaternary deposits contain a shallow aquifer, which is exploited primarily for irrigation in the Gafsa mining basin. This aquifer is essentially recharged by excess irrigation water coming from the deep CI and CT aquifers in the oases area (Hamed et al., 2014).

For “classic” PCA, OriginPro version 2023b (OriginLab Corporation, Northampton, MA, USA) was used to extract from the dataset the first two principal components using the correlation matrix (19 variables versus 33 samples; descriptive statistics in the Supplementary file 2a). The correlation matrix is simply the covariance matrix, standardized by

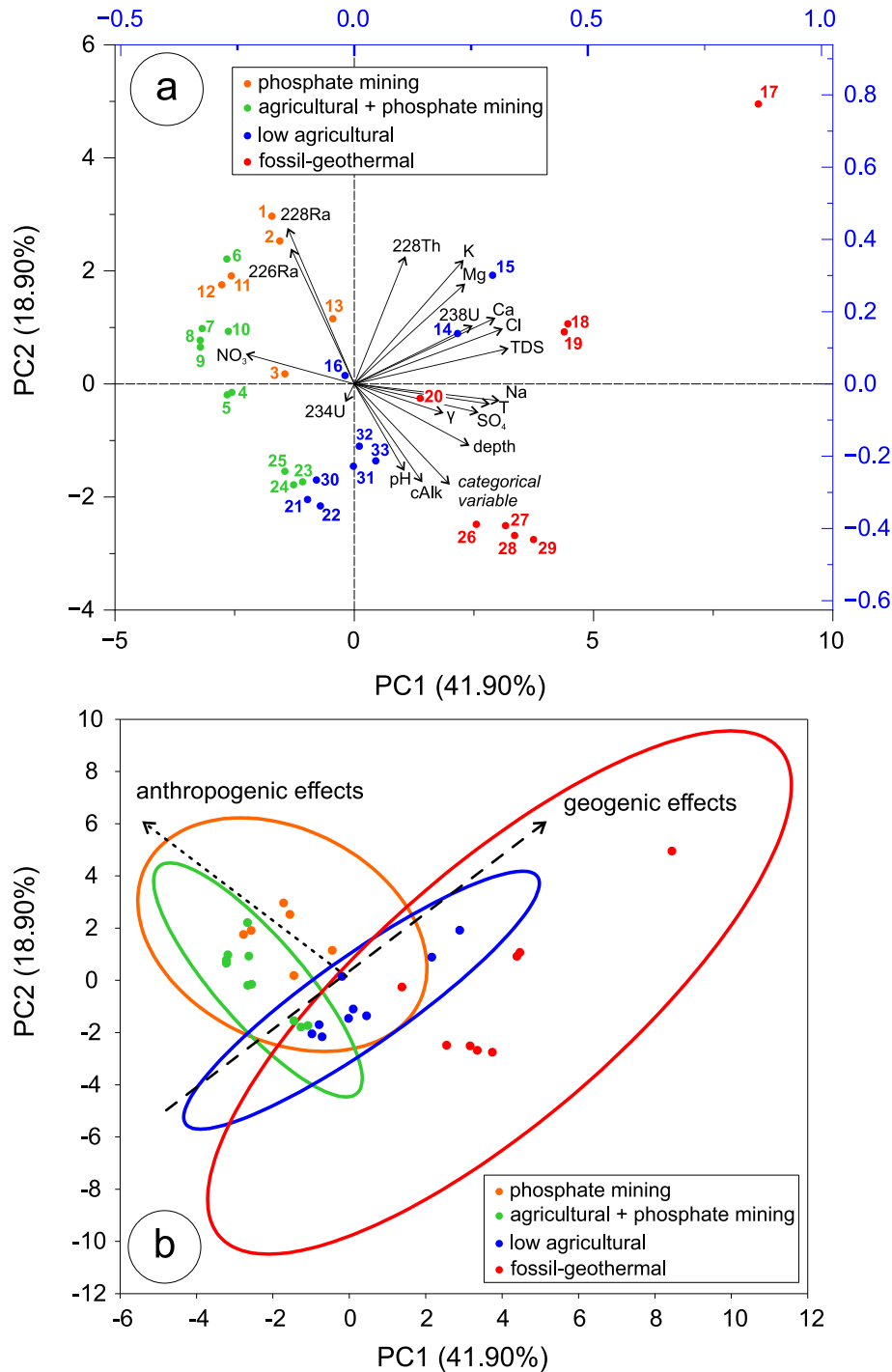


Fig. 2. a) Biplot of the first two principal components (PC1 and PC2, explaining 41.90 % and 18.90 % of the variance, respectively) extracted by the correlation matrix. Precipitation values in the area of the sampled springs. The biplot displays the variable loadings (eigenvectors, blue arrows; coordinates on the top and right axes) and the sample scores (colored dots differentiated on the basis of categorical variables -groundwater classes- and labelled with the groundwater sample numbers). Co-linear variable vectors indicate strong positive correlation, with the vector length proportional to the variable influence on the PC score. Sample proximity to a vector reflects variable influence on the sample. b) 95 % confidence ellipses of each group in the PCA score space: the ellipses edge colors correspond to those of the categorical variables (i.e., the four groundwater classes). The two ideal vectors distinguish the trend of the local groundwater divide: natural waters with a geogenic source of radioactivity (rightward dashed line) and polluted waters influenced by nitrate and radioactivity from anthropogenic activities such as phosphate mining and agriculture (leftward dotted arrow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

setting all variances equal to one (Wei, 2019).

A PCA using the covariance matrix was also performed. However, despite the higher variance explained by the first two principal components extracted from the covariance matrix (PC1 + PC2 = 92.62 %) compared to the correlation matrix PCA (PC1 + PC2 = 60.80 %) (Supplementary file 2b and c), the vectors associated with the radioactive elements remains indistinguishable in the covariance-based PCA. Indeed, they cluster near the centroid of the PCA biplot along with other chemical and physico-chemical variables (except for Na, Depth, SO₄, and Cl) (Supplementary file 2c). Consequently, the scores assigned to the samples influenced by these parameters are also indistinguishable. This is not surprising, as using the correlation matrix in PCA can be advantageous when the variables have very different variances, as in this case (Supplementary file 1). Standardizing the data, as is automatically done when using PCA and correlation matrix (Masnan et al., 2012), it ensures that no single variable dominates the analysis due to its scale. In contrast, using the covariance matrix might lead to a less balanced representation of the principal components, especially when there is significant variance disparity among the variables. We also used the robust PCA (rrcov package version 1.7–6 for RStudio, version 2024.04.2) (RStudio-Team, 2020). Robust PCA minimizes the influence of outliers using robust estimators, making it more reliable than classical PCA for noisy or extreme-value datasets. Its key strength is detecting meaningful structures hidden in noise (Filzmoser and Todorov, 2013; Hubert et al., 2005). However, since the results are entirely comparable to those obtained with covariance-based PCA, they will not be discussed further (Supplementary file 2c and d).

The principal components extracted from the correlation matrix can effectively discriminate samples that are most affected by anthropogenic impacts and show significant pollution from radium and nitrates (Fig. 2a). Specifically, the samples located mainly in the sector with negative PC1 and positive PC2 in the PCA biplot are characterized by (Fig. 2a): i) ²²⁶Ra activity and NO₃ concentrations up to eight times their respective drinking water guidelines (WHO, 2022); ii) shallow depth (depth < 200 m); iii) NW-SE oriented confidence ellipses (Fig. 2b). In contrast, the samples with minimal anthropogenic influence (low agricultural) and those from fossil/geothermal waters are of greater depth (depth > 200 m) and have NE-SW oriented confidence ellipses (Fig. 2b).

In groundwater from phosphate mining areas, as Gafsa's samples, the higher activity of radium than uranium could be related to their chemical and crystallographic properties. In particular, radium does not occupy regular lattice positions within uranium-bearing minerals (Burnett et al., 1988). Furthermore, it is well known that nearly all radium (mainly ²²⁶Ra) present in the ore ends up in the waste phosphogypsum during the production of phosphate fertilizers, and smaller quantities of U and Th isotopes (Fesenko et al., 2014).

The association between the ²³⁸U and Ca variable vectors to the deep fossil waters is attributed to the Ca-plagioclase sandstone of the aquifer and to the presence of oxidized waters rather than reduced ones, as the reduction from U(VI) to U(IV) would tend to immobilize uranium like the reduction of iron (Hamed et al., 2024; Smedley and Kinniburgh, 2023). This hypothesis is further supported by the relatively high concentrations of sulfate ions, as fossil waters in reduced environments typically exhibit very low sulfate concentrations due to its S(VI)-S(-II) reduction and its loss as H₂S gas or mineral sulfides (Boschetti et al., 2011).

4. Conclusion and ways forward

The application of PCA in this study has successfully distinguished groundwater samples impacted by anthropogenic activities, specifically from phosphate mining and agriculture, with elevated levels of radium and nitrate contamination. These contaminants often exceed safe drinking water guidelines, and their presence is more pronounced in shallow aquifers susceptible to pollution from agricultural runoff and mining activities. Accurate identification of pollution sources and

differentiation from the natural background is the crucial first step in effective mitigation and remediation. An additional step forward in PCA analysis in environments like this could involve incorporating the isotopic composition of nitrate, both as δ¹⁸O(NO₃) and δ¹⁵N(NO₃), which could more distinctly differentiate the various sources of nitrate pollution. Addressing nitrate and radium contamination in regions like the Gafsa basin requires targeted strategies. Phosphogypsum contaminated with radionuclides is mainly stored in open-air facilities, posing environmental challenges for air pollution. While its use in construction materials like cement or bricks is feasible (Ajam et al., 2009), concerns about its radioactivity limit widespread adoption. Phytoremediation offering a potential remediation solution for nitrate pollution (Guéblé et al., 2024; Mohammadzadeh and Hajiboland, 2022), though this approach may be challenging in extensive and arid areas (Zhao et al., 2022), and bioremediation for radionuclides (Martinez et al., 2014). However, advanced monitoring systems are crucial to track contaminant movement in hydrologically connected aquifers. Sustainable agricultural practices and alternatives to nitrogen-rich fertilizers could reduce nitrate input into groundwater. Finally, investigating the long-term effects of radium and uranium contamination on water quality and public health is essential to guide future environmental policies.

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CRedit authorship contribution statement

Tiziano Boschetti: Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Younes Hamed:** Writing – review & editing, Visualization, Project administration, Methodology, Investigation, Funding acquisition, Data curation. **Rihab Hadji:** Validation, Resources, Investigation, Data curation. **Maurizio Barbieri:** Validation, Supervision, Methodology, Conceptualization. **Matteo Gentilucci:** Validation, Supervision, Methodology, Conceptualization. **Mattia Rossi:** Writing – original draft, Software, Formal analysis. **Rayan Khalil:** Writing – original draft, Visualization, Investigation, Data curation. **Shuhab D. Khan:** Visualization, Investigation, Data curation. **Bassem Asghar:** Visualization, Investigation, Data curation. **Abdulrasoul Al-Omran:** Validation, Investigation, Data curation. **Elimame Elaloui:** Validation, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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